

## ***Interactive comment on “Improved global modelling of HO<sub>x</sub> recycling in isoprene oxidation: evaluation against the GABRIEL and INTEX-A aircraft campaign measurements” by T. Stavrakou et al.***

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We thank Mike Jenkin for his thoughtful comments. In the following, we address the concerns raised. Reviewer's comments are *italicized*.

*1) The results show that LIM0 has the potential to close the model-measurement discrepancy gap for HO<sub>x</sub>, but does not provide absolute proof that the mechanism is correct. It is possible that there may be other currently unidentified and unrepresented contributors to HO<sub>x</sub> formation and recycling, such that getting good model-*

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*measurement agreement for HO<sub>x</sub> does not in itself constitute validation (even if the result is informative and encouraging). In a final statement on page 16571, the authors are careful to indicate that there are uncertainties in the mechanism and that further experimental work is essential to validate it. This crucial requirement should probably be given even more emphasis, including mention in the Abstract.*

We agree with the reviewer on the importance of uncertainties and on the need for further experimental work. A new sentence has been added to the abstract to emphasize this point: "Experimental confirmation and quantification is urgently needed for the formation of HPALDs and for their fast OH-generating photolysis."

*2) In the final sensitivity test, S8, a case is made for changes in the isoprene emission rate which result in a final impressive agreement between modelled and observed concentrations for the series of species presented in Table 3. If these changes in emission rate are considered justifiable, should they be implemented at the start of the process so that the results of each mechanistic sensitivity test can be compared more directly with the observations?*

The isoprene emission changes of the sensitivity test S8 result in a nice model/data agreement against aircraft observations only for the specific chemical mechanism used (LIM0 with halved k(1,6) and isoprene/OH segregation factor equal to 0.9). For example, implementing the same emission changes to simulations S0–S4 would lead to a strong isoprene overestimation against GABRIEL data, and to an underestimation of these concentrations against INTEX-A measurements. In other terms, emission optimisation is clearly model dependent. Therefore, adopting the unmodified emission estimates of the widely-used MEGAN emission inventory seemed to be the least arbitrary choice we could do.

*3) The large flux predicted for formation of the HPALD species by operation of LIM0 logically results in a corresponding reduction in the formation of conventional isoprene*

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products (hydroperoxides, nitrates, MVK and MACR), as presented in Tables 2 and 3. Implementation of LIM0 therefore generally seems to worsen model-measurement agreement for MVK+MACR during GABRIEL (Table 3), although the final comparison in S8 with the elevated isoprene emission rate and a reduced rate for  $k(1,6)$  (0.64 ppb simulated vs. about 1 ppb observed) is considered acceptable by the authors. My concern here is that this underestimation is despite the fact that MVK+MACR formation from LIM0 may already be artificially too high. My reasoning for this relates to the use of the yield of MVK+MACR reported in the chamber study of Paulot et al. (2009) to optimise  $k(1,5)$  on page 16559, with the clear assumption that there are no other sources of MVK+MACR under the chamber conditions employed. The resultant optimised value is substantially higher than that originally reported by Peeters et al. (2009), and some two orders of magnitude greater than reported recently in another theoretical study (da Silva et al., 2010), which should really be cited and discussed in the present paper. Given that the initial relative formation rate of RO<sub>2</sub> and HO<sub>2</sub> in the Paulot study is about 3:1, it is highly likely that a major contribution to MVK+MACR formation comes from the self- and cross- reactions of the RO<sub>2</sub> species, which are able to compete partially with RO<sub>2</sub>+HO<sub>2</sub>. The RO<sub>2</sub> self- and cross- reactions are stated to be represented in the global calculations (page 16561), but are not apparently considered in appraisal of a chamber experiment, where they are likely to be more important. In my opinion, the high rate applied to  $k(1,5)$  is therefore probably not justified, and the formation of MVK+MACR simulated with LIM0 may be artificially elevated. A reduction in the yield would clearly worsen the model-measurement agreement for MVK+MACR in Table 3, suggesting that this aspect of performance may not be validated by the present comparison. Please can the authors comment.

As described in Peeters and Müller (PCCP, in press, 2010), the rate of the 1,5-H shifts  $k(1,5)$  in LIM0 has been adjusted using the yield of MVK+MACR measured by Paulot et al. (2009), allowing for 2–3% MVK+MACR formation from reactions of ISOP-OH-OO with peroxy radicals. The relatively unimportant role of the cross reactions of peroxy

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radicals in Paulot et al. (2009) is expected due to their high HO<sub>2</sub> concentrations (ca.  $3\text{--}5 \cdot 10^9 \text{ cm}^{-3}$ ) and the high  $k(\text{RO}_2+\text{HO}_2)$  of  $1.7 \cdot 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ , compared to the much lower  $k$ 's for self- and cross reactions of the RO<sub>2</sub>'s. This was indeed evidenced by the very low diol yields (2%) measured by Paulot et al. in comparison to other products as MVK and MACR (see the Paulot et al. paper and supporting material). It is important to note that the 12% MVK+MACR yield is reported by Paulot et al. for larger reaction times, when the NO<sub>x</sub> is mostly sequestered as nitrates. After 3 hours, the relative RO<sub>2</sub> and HO<sub>2</sub> formation rate has decreased from the initial 3:1 ratio to  $(8.4 \cdot 10^7 - 2.1 \cdot 10^7) : (5.9 \cdot 10^7 + 4.0 \cdot 10^7) = 0.64:1$ , where we account for the 25% of the formed peroxy quickly resulting in HO<sub>2</sub> + HPALDs, whose fast photolysis forms another 0.9 HO<sub>2</sub> (Peeters and Müller, 2010).

The much lower  $k(1,5\text{-H})$  rates predicted by da Silva et al. have been also addressed in Peeters and Müller (2010). On one hand, the da Silva et al. levels of theory are lower than the CBS-APNO level of Peeters et al. (2009), and as mentioned in the latter paper, the computed energy barrier for this process show a decreasing trend when using higher levels of theory. Secondly, da Silva et al. calculate a too low tunneling factor, as they consider tunneling only for the endothermic "first step" to the oxy radical intermediate, whereas the reaction is in fact a concerted process proceeding in a single step that is quasi-thermoneutral (see Peeters and Müller, 2010). Note also that it was already anticipated by Peeters et al. (2009) that the actual  $k(1,5\text{-H})$  is likely higher than the first-principles predictions.

4) As discussed by Peeters et al. (2009), the formation of the HPALD species (and HO<sub>2</sub>) following the 1,6 H-shift isomerisation of the *d*-hydroxy RO<sub>2</sub> radicals requires reaction of a hydroxy-allyl radical with O<sub>2</sub>. Peeters et al. (2009) reasonably argue that the necessary  $\alpha$ -O<sub>2</sub> addition dominates over  $\gamma$ -O<sub>2</sub> addition. However, in view of the experimental observation of formation of epoxy compounds from similar structures by Paulot et al. (2009), I would be interested to know the authors' view on whether direct elimination of OH in conjunction with formation of an epoxy compound

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(see Fig.1 below) could compete with alpha- O2 addition. This would provide a direct route to OH recycling (although the HOx chain-branching aspect of the mechanism would be lost).

The Z-delta-peroxy 1,6-H shift is exothermic for only about 5 to 10 kcal/mol, far less than the ca. 30 kcal/mol internal energy the product radical requires to promptly overcome the 11 to 12 kcal/mol energy barrier to epoxide formation (Paulot et al., 2009) before collisional stabilization (followed by reaction with O<sub>2</sub>). The thermal reaction of the stabilized product radical to epoxide is at least three orders of magnitude slower than reaction with O<sub>2</sub>. Note that in the Paulot et al. mechanism to epoxides, the reacting radical has acquired the necessary internal energy by addition of OH to the unsaturated hydroperoxide precursor.

*Minor comments:*

*Abstract, line 6: I would suggest replacing "validated" by "evaluated" (as in the paper title).*

*Page 16564, line 28: The comment about the yields of HPALDs being lower in polluted regions seems to be presented as if it is a surprising result, whereas it is surely as expected. Perhaps "interestingly" could be replaced by something like "logically".*

Changed as suggested.

References:

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